

CLAIMS

1. A process for producing an alumina coating composed mainly of α -type crystal structure, comprising, when forming an alumina coating composed mainly of α -type crystal structure on a base material having a primary coating preliminarily formed thereon, forming a hard coating composed of a metal component containing Al and Ti as unavoidable elements and a compound of B, C, N, O, etc. as said primary coating, oxidizing said hard coating to form an oxide-containing layer, and then forming an alumina coating composed mainly of α -crystal structure on said oxide-containing layer.

2. The process according to claim 1, wherein the outermost surface side of said oxide-containing layer is substantially composed of alumina.

3. The process according to claim 1, wherein said primary coating is composed of TiAlN.

4. The process according to claim 1, wherein said primary coating is composed of a nitride, cemented carbide, carbonitride, boride, nitroxide, or carbonitroxide containing Al and Ti, and at least one element selected from the group consisting of elements of the groups IVa (except Ti), Va and VIa and Si as unavoidable components.

5. The process according to claim 1, wherein said primary coating is composed of TiAlCrN.

6. A process for producing an alumina coating composed mainly of α -type crystal structure, comprising, when forming an alumina coating composed mainly of α -type crystal structure on a base material having a primary coating preliminarily formed thereon, forming a hard coating

composed of a metal component containing Al as an unavoidable element and a compound of B, C, N, O, etc. as said primary coating, oxidizing said hard coating to form an oxide-containing layer, and then forming an alumina coating composed mainly of α -type crystal structure on said oxide-containing layer.

7. The process according to claim 6, wherein said primary coating is composed of a nitride, cemented carbide, carbonitride, boride, nitroxide, or carbonitroxide containing Al and at least one element selected from the group consisting of elements of the groups IVa, Va and VIa and Si as unavoidable components.

8. A process for producing an alumina coating composed mainly of α -type crystal structure, comprising, when forming an alumina coating composed mainly of α -type crystal structure on a base material having a primary coating preliminarily formed thereon, forming a hard coating composed of a metal whose standard free energy for oxidation generation is greater than that of aluminum and a compound of B, C, N, O, etc. as said primary coating, oxidizing said hard coating to form an oxide-containing layer, and then forming an alumina coating composed mainly of α -type crystal structure on said oxide-containing layer.

9. The process according to claim 8, wherein a hard coating composed of Ti that is a metal whose standard free energy for oxide formation is greater than that of aluminum and a compound of B, C, N, O, etc. is formed as said primary coating.

10. The process according to claim 8, wherein one or two or more laminate layers selected from the group consisting of TiN, TiC and TiCN are

formed as said primary coating.

11. The process according to claim 8, wherein a composition gradient layer of both material constituting elements to be connected is formed in a connecting interface between said hard coating and said base material, or between said hard coatings.

12. The process according to claim 8, wherein a titanium oxide-containing layer is formed as said oxide-containing layer and, in the following formation of alumina, an alumina coating is formed while being accompanied by reduction of the titanium oxide on the surface of said layer.

13. The process according to claim 8, wherein a TiO_2 -containing layer is formed as said oxide-containing layer and, in the following formation of alumina, an alumina coating is formed while being accompanied by reduction of TiO_2 to Ti_3O_5 on the surface of said layer.

14. A process for producing an alumina coating composed mainly of α -type crystal structure comprising, when producing an alumina coating composed mainly of α -type crystal structure on a base material (including a base material having a primary coating preliminarily formed thereon), forming at least one of the following coatings (a)-(c) prior to the deposition process of alumina, oxidizing the resulting surface, and then forming an alumina coating:

(a) A coating composed of a pure metal or alloy:

(b) A coating composed mainly of a metal solid-dissolving nitrogen, oxygen, carbon or boron:

(c) A coating composed of a metal nitride, oxide, cemented carbide or boride containing nitrogen, oxygen, carbon or boron insufficient to a

stoichiometric composition.

15. The process according to claim 1, 6, 8 or 14, wherein said oxidation treatment is carried out in an oxidizing gas-containing atmosphere while retaining a base material temperature at 650-800°C.

16. The process according to claim 1, 6, 8 or 14, wherein the formation of said alumina coating composed mainly of α -type crystal structure is performed by a PVD method.

17. The process according to claim 1, 6, 8 or 14, wherein the process of oxidizing the surface of said primary coating and the process of forming said alumina coating composed mainly of α -type crystal structure are carried out within the same apparatus.

18. The process according to claim 1, 6, 8 or 14, wherein the process of forming said primary coating, the process of oxidizing the surface of said primary coating, and the process of forming said alumina coating composed mainly of α -type crystal structure are successively carried out within the same apparatus.

19. A clad member excellent in wear resistance and heat resistance comprising an alumina coating composed mainly of α -type crystal structure formed on the surface, said alumina coating being produced by the process according to claim 1, 6, 8 or 14.

20. A laminate coating excellent in wear resistance and heat resistance including a hard coating composed of a metal component containing Al and Ti as unavoidable elements and a compound of B, C, N, O, etc., said laminate coating further comprising an oxide-containing layer formed by oxidizing said hard coating, and an alumina coating composed

mainly of α -type crystal structure formed on said oxide-containing layer.

21. The laminate coating according to claim 20, wherein the outermost surface side of said oxide-containing layer is substantially composed of alumina.

22. The laminate coating according to claim 20, wherein said hard coating is composed of TiAlN.

23. The laminate coating according to claim 20, wherein said hard coating is composed of a nitride, cemented carbide, carbonitride, boride, nitroxide, or carbonitroxide containing Al and Ti, and at least one element selected from the group consisting of elements of the groups IVa (except Ti), Va and VIa and Si as unavoidable components.

24. The laminate coating according to claim 20, wherein said hard coating is composed of TiAlCrN.

25. A laminate coating excellent in wear resistance and heat resistance including a hard coating composed of a metal component containing Al as an unavoidable element and a compound of B, C, N, O, etc., the laminate coating further comprising an oxide-containing layer with the outermost surface side substantially composed of alumina, said oxide-containing layer being formed by oxidizing said hard coating, and an alumina coating composed mainly of α -type crystal structure formed on said oxide-containing layer.

26. The laminate coating according to claim 25, wherein said hard coating is composed of a nitride, cemented carbide, carbonitride, boride, nitroxide, or carbonitroxide containing Al and at least one element selected from the group consisting of elements of the groups IVa, Va and VIa and Si as

unavoidable components.

27. The laminate coating according to claim 20 or 25, wherein the alumina coating formed on said oxide-containing layer has 70% or more α -crystal structure.

28. A tool clad with laminate coating comprising a laminate coating according to claim 20 or 25 formed on the surface.

29. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising successively executing a process for forming at least any one of the following coatings (a)-(c) as an intermediate layer, a process for oxidizing the surface of said intermediate layer, and a process for forming an alumina coating composed mainly of α -type crystal structure within the same apparatus:

(a) A coating composed of a pure metal or alloy:

(b) A coating composed mainly of a metal solid-dissolving nitrogen, oxygen, carbon or boron:

(c) A coating composed of a metal nitride, oxide, cemented carbide or boride containing nitrogen, oxygen, carbon or boron insufficient to a stoichiometric composition.

30. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising successively executing a process for forming a primary coating on a base material, a process for forming at least any one of the following coatings (a)-(c) on the surface of said primary coating as an intermediate layer, a process for oxidizing the surface of said intermediate layer, and a process for forming an alumina coating composed mainly of α -type crystal structure within the

same apparatus:

(a) A coating composed of a pure metal or alloy:

(b) A coating composed mainly of a metal solid-dissolving nitrogen:
oxygen, carbon or boron:

(c) A coating composed of a metal nitride, oxide, cemented carbide or boride containing nitrogen, oxygen, carbon or boron insufficient to a stoichiometric composition.

31. A process for producing an alumina coating composed mainly of α -type crystal structure on a sintered cBN base material composed of a binder phase and a cubic boron nitride dispersed layer, comprising oxidizing the surface of said sintered cBN base material, and then forming an alumina coating.

32. The process according to claim 31, wherein said binder phase contains one or more selected from the group consisting of TiC, TiN, TiCN, AlN, TiB₂ and Al₂O₃.

33. The process according to claim 31, wherein said oxidizing step is performed in an oxidizing gas-containing atmosphere while retaining the base material temperature at 650-800°C.

34. The process according to claim 31, wherein formation of said alumina coating composed mainly of α -type crystal structure is performed at a base material temperature of 650-800°C by use of a physical vapor deposition method.

35. A member clad with an alumina coating composed mainly of α -type crystal structure which is a clad member including a sintered cBN composed of a binder phase and a cubic boron nitride dispersed phase, and

an alumina coating of α -type crystal structure applied thereto, said member further comprising an oxide-containing layer interposed in the interface between said sintered cBN base material and said alumina coating.

36. The member according to claim 35, wherein said binder phase contains one or more selected from the group consisting of TiC, TiN, TiCN, AlN, TiB₂ and Al₂O₃.

37. The member according to claim 35, wherein said binder phase is contained in a ratio of 1-50 vol% to the whole sintered body.

38. The member according to claim 35, wherein said alumina coating composed mainly of α -type crystal structure has a residual stress of compression.

39. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising, when producing a clad member including a sintered cBN composed of a binder phase and a cubic boron nitride dispersed phase clad with an alumina coating composed mainly of α -type crystal structure, successively executing a process for oxidizing the surface of said sintered cBN and a process for forming said alumina coating composed mainly of α -type crystal structure within the same deposition apparatus.

40. A process for producing an alumina coating composed mainly of α -type crystal structure on a base material (including a base material having a primary coating preliminarily formed thereon), comprising gas ion-bombarding the surface of said base material, oxidizing the resulting surface, and then forming an alumina coating.

41. The process according to claim 40, wherein either one or more of a

compound of one or more elements selected from the group consisting of elements of the groups 4a, 5a and 6a of the periodic table, Al, Si, Fe, Cu and Y and one or more elements of C, N, B and O and a mutual solid solution of these compounds is formed as said primary coating.

42. The process according to claim 40, wherein one or more selected from the group consisting of Ti(C,N), Cr(C,N), TiAl(C,N), CrAl(C,N) and TiAlCr(C,N) is formed as said primary coating.

43. The process according to claim 40, wherein said base material is a steel product, a cemented carbide, a cermet, a sintered cBN or a sintered ceramic.

44. The process according to claim 40, wherein said gas ion bombardment treatment is performed within a vacuum chamber while applying a voltage to said base material in a gas plasma.

45. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising successively executing a process for forming a primary coating on a base material, a process for gas ion-bombarding the surface of said primary coating, a process for oxidizing the resulting surface, and a process for forming an alumina coating composed mainly of α -type crystal structure within the same apparatus.

46. The process according to claim 45, wherein one or more selected from the group consisting of Ti(C,N), Cr(C,N), TiAl(C,N), CrAl(C,N) and TiAlCr(C,N) is formed as said primary coating.

47. A process for producing an alumina coating composed mainly of α -type crystal structure on a base material (including a base material having

a primary coating preliminarily formed thereon), comprising metal ion-bombarding the surface of said base material, oxidizing the resulting surface, and then forming an alumina coating.

48. The process according to claim 47, wherein said metal ion bombardment treatment is performed by generating a metal plasma in a vacuum chamber while applying a voltage to said base material.

49. The process according to claim 47, wherein said metal ion bombardment treatment is performed by generating a plasma of Cr or Ti from a vacuum arc evaporation source while applying a voltage to said base material in the vacuum chamber.

50. The process according to claim 47, wherein said oxidizing step is carried out in an oxidizing gas-containing atmosphere while retaining the base material temperature at 650-800°C.

51. A member clad with an alumina coating composed mainly of α -type crystal structure including an alumina coating composed mainly of α -type crystal structure formed on a base material (including also a base material having a primary coating preliminarily formed thereon), wherein a concentration gradient layer in which the concentration of a metal used for a metal ion bombardment treatment is gradually increased toward the surface layer side is present in the vicinity of the surface of said base material, and an oxide-containing layer and said alumina coating composed mainly of α -type crystal structure are formed successively on the surface side of said concentration gradient layer.

52. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising successively

executing a process for metal ion-bombarding the surface of a base material, a process for oxidizing the resulting surface, and a process for forming an alumina coating composed mainly of α -type crystal structure within the same apparatus.

53. A process for producing a member clad with an alumina coating composed mainly of α -type crystal structure, comprising successively executing a process for forming a primary coating on a base material, a process for metal ion-bombarding the surface of said primary coating, a process for oxidizing the resulting surface, and a process for forming an alumina coating composed mainly of α -type crystal structure within the same deposition apparatus.

54. The process according to claim 53, wherein said primary coating consists of one or more of a compound of one or more elements selected from the group consisting of elements of the groups 4a, 5a and 6a of the periodic table, Al, Si, Cu and Y with one or more elements of C, N, B, and O, a mutual solid solution of such compounds, or a single body or compound composed of one or more elements of C, N, and B.

55. The process according to claim 53, wherein said base material is a steel product, a cemented carbide, a cermet, a sintered cBN, a sintered ceramic, crystalline diamond or a Si wafer.

56. An alumina coating of α -type crystal structure formed on a base material (including also a base material having a primary coating preliminarily formed thereon) by a physical vapor deposition method, wherein, when the crystal structure of said alumina coating is observed by cross-sectional transmission electron microscopy (magnification: 20000

times), at least a coating growth start part is formed of alumina crystals of minute structure, and crystal structures other than α -type crystal structure are not substantially observed in said minute crystal area.

57. The alumina coating according to claim 56, wherein said alumina crystals of minute structure have crystal grains of $0.3\ \mu\text{m}$ or less within the range from the initial stage of growth to $0.5\ \mu\text{m}$ in the thickness direction.

58. The alumina coating according to claim 56, wherein crystal structures other than α -type crystal structure are not substantially observed all over said alumina coating.

59. The alumina coating according to claim 56, wherein alumina of α -type crystal structure grows in a columnar shape on the surface side of said coating.

60. The alumina coating according to claim 56, wherein a film thickness of said alumina coating is $0.5\text{-}20\ \mu\text{m}$.

61. A physical vapor deposition apparatus, comprising a vacuum chamber, a base material holder for retaining a plurality of base materials, said holder being disposed rotatably in said vacuum chamber, an introduction mechanism of inert gas and oxidizing gas to said vacuum chamber, a plasma source disposed in a position opposed to said base material holder, a sputtering evaporation source disposed in a position opposed to said base material holder, a radiation type heating mechanism disposed in a position opposed to said base material holder so as to be capable of heating said base material, and a bias power supply connected to said base material holder so as to be capable of applying a negative pulse bias voltage to said base material holder.

62. The physical vapor deposition apparatus according to claim 61, wherein an arc evaporation source is disposed in a position opposed to said base material holder instead of said plasma source or in addition to said plasma source.

63. The physical vapor deposition apparatus according to claim 61, wherein said radiation type heating mechanism comprises a cylindrical heating source disposed concentrically with the rotating center of said base material holder, and a flat heating source disposed on a side surface of said base material holder.

64. The physical vapor deposition apparatus according to claim 61, wherein said vacuum chamber has a sectional shape of any one of square, hexagonal and octagonal shapes, said radiation type heating mechanism comprises a cylindrical heating source disposed concentrically with the rotating center of said base material holder and a flat heating source disposed on a side surface of said base material holder, and said sputtering evaporation source and said flat heating source are disposed each in pairs on mutually opposed inside surfaces of said vacuum chamber, respectively.

65. The physical vapor deposition apparatus according to claim 61, wherein said vacuum chamber has a hexagonal or octagonal sectional shape, said radiation type heating mechanism comprises a cylindrical heating source disposed concentrically with the rotating center of said base material holder and a flat heating source disposed on a side surface of said base material holder, and said sputtering evaporation source, said flat heating source and an arc evaporation source are disposed each in pairs on mutually opposed inside surfaces of said vacuum chamber, respectively.

66. The physical vapor deposition apparatus according to claim 61, wherein said plasma source is a filament for emission of thermal electron disposed within said vacuum chamber so that its longitudinal direction is opposed adjacently to said base material holder.

Table 1

	Hard Coating	Oxidation Process		Deposition Process of Alumina Coating			Measurement Result of Alumina Coating		
		Substrate Temp.	Heating Time	Power	Number of sputtering sources used	Substrate Temp.	Film Thickness	I α /I γ	Crystal Structure
Inventive Case 1	TiAlN	780°C	20 min	3 kW	2	780°C	2 μ m	γ -peak detected* ¹	α -type
Comparative Case 1	TiAlN+CrN						2 μ m	γ -peak detected* ¹	α -type
Inventive Case 2	TiAlN	750°C	20 min	3 kW	1	770°C	1.15 μ m	2.8	α -type: main, γ -type: sub
Inventive Case 3	TiAlCrN						1.15 μ m	2.9	α -type: main γ -type: sub
Inventive Case 4	TiAlN	740°C	60 min	3 kW	1	770°C	0.9 μ m	γ -type detected* ¹	α -type
Comparative Case 2	TiAlN	635°C	20 min	3 kW	1	670°C	1.3 μ m	1.4	Mix of α -type and γ -type
Comparative Case 3	TiAlN	580°C	20 min	3 kW	2	590°C	2 μ m	α -type detected* ²	γ -type

*1: Peak of $2\theta = 19.4502^\circ$ is not detected.*2 Peak of $2\theta = 25.5761^\circ$ is not detected.

Table 2

	Hard Coating	Oxidation Process		Deposition Process of Alumina Coating			Measurement Result of Alumina Coating		
		Substrate Temp.	Heating Time	Substrate Temp.	Average Discharge Power (total of 2)	Deposition Time	Film Thickness	$I\alpha/I\gamma$	Crystal Structure
Inventive Case 1'	TiN	760°C	20 min	770°C	5.6 kW	3 hr	2 μ m	γ -peak not detected*	α -type: main γ -type: sub
Inventive Case 2'	TiCN							γ -peak not detected*	α -type: main γ -type: sub
Reference Case	CrN							$I\alpha/I\gamma=6.4$	α -type: main γ -type: sub

* Peak of $2\theta=19.4502^\circ$ is not detected